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<b>(21) International Application Number:</b> PCT/GB99/02954 <b>(22) International Filing Date:</b> 6 September 1999 (06.09.99)  <b>(30) Priority Data:</b> 9820608.9 23 September 1998 (23.09.98) GB  <b>(71) Applicant (for all designated States except US):</b> IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chem- ical House, Millbank, London SW1P 3JF (GB).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> WARD, Andrew, Mark [GB/GB]; 88 Beaconsfield Road, Norton, Stockton on Tees, Cleveland TS20 1JN (GB).  <b>(74) Agents:</b> GRATWICK, Christopher et al.; ICI Group Intellectual Property, P.O. Box 90, Wilton, Middlesbrough, Cleveland TS90 8JE (GB).		<b>(81) Designated States:</b> AU, BR, CA, CN, CZ, ID, IN, JP, KR, US, ZA, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR THE PRODUCTION OF HYDROGEN  <b>(57) Abstract</b>  A high temperature shift process using an iron oxide-containing catalyst wherein the feed gas is contacted with an iron-free, copper-containing, catalyst at an inlet temperature in the range 280–370°C before contact with the iron oxide-containing catalyst in order to effect some shift reaction and thus avoid conditions conducive to over-reduction of the iron oxide containing catalyst.		

## PROCESS FOR THE PRODUCTION OF HYDROGEN

This invention relates to hydrogen and in particular to the production of a hydrogen-containing gas stream from a carbonaceous feedstock. Such processes are well known and involve the steam reforming of a hydrocarbon feedstock, e.g. natural gas, or of a hydrocarbon derivative e.g. methanol, or the partial oxidation, using an oxygen-containing gas, e.g. substantially pure oxygen, air, or oxygen-enriched or oxygen-depleted air, of a hydrocarbon, or hydrocarbon derivative, feedstock or of a solid carbonaceous feedstock such as coal. Such gas generation processes produce a gas stream at a relatively high temperature, normally above 700°C, containing hydrogen, carbon monoxide, and steam, and usually also some carbon dioxide. The gas stream will normally contain some methane together with any inert gases, e.g. nitrogen, that were present in the reactants.

In order to increase the hydrogen content of the gas stream it is well known to subject the gas stream to the shift reaction



by passage of the gas through a bed of a suitable catalyst.

The forward shift reaction equilibrium is favoured by low temperatures. However since the reaction is exothermic, unless steps are taken such as cooling the gas while in the catalyst bed, the temperature rise occurring if the feed contains a substantial amount of carbon monoxide is often such that low outlet temperatures can not be achieved and/or the catalysts effective at low outlet temperatures are rapidly de-activated. For this reason the shift reaction is often carried out in two stages; the first stage (high temperature shift) employing a catalyst comprising iron oxide, e.g. an iron oxide/chromia catalyst, and, after some form of inter-bed cooling, the second stage (low temperature shift) employing a copper-containing catalyst.

In use, the iron oxide in the high temperature shift catalyst may be reduced to a state wherein the catalyst tends to catalyse the Fischer-Tropsch reaction forming hydrocarbons. Reduction of the iron oxide to such a state is thus desirably avoided. We have found that for high temperature shift using conventional iron oxide/chromia catalysts and conventional high temperature shift exit temperatures, e.g. in the range of about 350-500°C, the risk of hydrocarbon formation depends upon the molar ratio of carbon monoxide to carbon dioxide and the proportion of steam in the shift inlet gas. The risk of hydrocarbon formation increases as the carbon monoxide to carbon dioxide ratio increases: however provided sufficient steam is present, the risk may be minimised.

The gasification stage used to produce the shift inlet gas is normally operated at a pressure in the range 5 to 50 bar abs., and in particular in the range 10 to 40 bar abs. The temperature at which the gasification stage is effected will normally be in the range 700 to 1200°C, particularly 750 to 1100°C.

The carbon monoxide to carbon dioxide molar ratio and the proportion of steam will depend on the conditions employed in the gasification stage, i.e. the reforming or partial oxidation stage. Increasing the outlet temperature, increasing the pressure, and/or decreasing

characterised in that, prior to contact with the iron oxide-containing catalyst, the gas stream is contacted with an iron-free, copper-containing, catalyst at an inlet temperature in the range 280-370°C.

Iron-free, copper-containing, catalysts are normally employed for the so-called "low-  
5 temperature" shift reaction which often follows a stage of high temperature shift reaction. Normally catalysts containing a substantial proportion of copper are not employed at temperatures above about 300°C as the copper tends to sinter and so the catalyst loses activity. However, in the present invention, although some sintering and loss of activity will inevitably occur, the copper- containing catalyst is not required to effect shift to near equilibrium  
10 but only to effect some degree of shifting to modify the carbon monoxide to carbon dioxide ratio so that the problem of undue reduction of the subsequent iron oxide-containing catalyst and consequent Fischer-Tropsch reactions is avoided. Furthermore, although the inlet temperature to the preliminary shift stage is relatively low for a high temperature shift reaction, it is high for a shift reaction employing a catalyst containing a substantial proportion of copper, and this  
15 relatively high inlet temperature compensates for the loss of activity of the copper catalyst.

Copper-containing catalysts that may be employed include any of those well known for the methanol synthesis or the low temperature shift reaction. Typically the catalyst comprises the product of reducing pellets formed from a calcined composition of co-precipitated copper, zinc and aluminium and/or chromium compounds, e.g. oxides, hydroxides or basic carbonates.  
20 Often such catalysts contain more than 20% by weight of copper. Other components such as magnesium or manganese compounds may be incorporated. In a preferred system however, the copper- containing catalyst is the product of reducing a catalyst precursor comprising copper compounds supported on a material such as alumina or a calcium aluminate cement. Such a precursor may be produced by impregnating the support with a solution of a thermally  
25 decomposable copper compound, and optionally other components such as zinc, magnesium, aluminium and/or chromium compounds, followed by calcination of the impregnated support to decompose the copper compound, and possibly other components, to the oxidic state. Alternatively the support material may be coated with a slurry of precipitated, thermally decomposable, copper compounds, and possibly other components as aforesaid, dried, and  
30 then calcined to convert the thermally decomposable compounds to the oxidic form. Preferably such catalysts, after reduction, contain 3 to 15% by weight of copper. The use of such catalysts made by impregnating or coating a support is advantageous where the copper- containing catalyst is employed as a preliminary catalyst bed in the same vessel as the conventional iron oxide-containing high temperature shift catalyst. The catalyst may be in the  
35 form of a random packed bed of pellets of the support, which may be a macroporous foam as described in US 4 810 685, or monolithic, e.g. a honeycomb or a macroporous foam as aforesaid, to which the catalytic material has been applied, for example by impregnation or coating. The use of a macroporous foam as a support may be advantageous in certain cases as will be described hereinafter. One method of forming suitable impregnated catalysts

copper-containing, catalyst to effect shifting of 5 to 15% of the carbon monoxide present in the shift inlet gas. The temperature rise will generally be less than about 50°C and usually below 30°C.

Following the preliminary shift reaction, the gas mixture then undergoes the shift reaction over the iron oxide-containing high temperature shift catalyst. Although the inlet temperature to the iron-free, copper-containing, catalyst may be lower than is usually employed for high temperature shift catalysts, the exothermic reaction occurring over the iron-free, copper-containing, catalyst increases the temperature to a level at which the conventional iron oxide-containing shift catalyst is active. If, as is usual, the high temperature shift reaction over the iron oxide-containing catalyst is effected adiabatically, the temperature and carbon monoxide content of the gas leaving the high temperature shift reaction will depend on the composition of the shift inlet gas and how closely the shift equilibrium is approached. However the carbon monoxide content of the gas leaving the high temperature shift reaction is typically in the range 2-5% by volume (on a dry basis) and the outlet temperature will in the range 350-500°C. If desired, the shifted gas can be cooled and subjected to low temperature shift, e.g. at an outlet temperature in the range 200-280°C, using conventional low temperature shift catalysts.

Since the iron-free, copper-containing, preliminary shift catalyst can effect a significant amount of shift reaction, the volume of iron oxide-containing high temperature shift catalyst employed can be decreased. Typically up to 10% of the volume of iron oxide-containing high temperature shift catalyst may be replaced by the iron-free, copper-containing catalyst. Preferably the amount of iron-free, copper-containing, catalyst employed is 3-5% by volume of the iron oxide-containing catalyst. Conventional iron oxide-containing high temperature shift catalysts are usually operated at a wet gas space velocity in the range 2500 to 5000 h<sup>-1</sup>, although some modern, highly active, iron oxide-containing, high temperature shift catalysts have been operated at higher wet gas space velocities, e.g. up to about 7500 h<sup>-1</sup>. Operation at an overall wet gas space velocity of 5000 h<sup>-1</sup> but with replacement of 5% by volume of the conventional, iron oxide-containing, high temperature shift catalyst by an iron-free, copper-containing, catalyst in accordance with the present invention means that the iron-free, copper-containing, catalyst is operating at a wet gas space velocity of 100000 h<sup>-1</sup>. Preferably the iron-free, copper-containing, catalyst is operated at a wet gas space velocity of at least 20000 h<sup>-1</sup>, particularly at least 50000 h<sup>-1</sup>. It will be appreciated that the volume of the iron-free copper-containing catalyst that is required will depend, inter alia, on the amount of copper in a given volume of catalyst and the accessibility of that copper to the process gas. Preferably the amount of iron-free copper-containing catalyst employed is such that the wet gas flow rate is in the range 250-3000 litres (at NTP) of wet gas per g of copper in the catalyst per hour.

In many processes, e.g. where the shift reaction follows production of a crude gas by steam reforming and/or partial oxidation, heat is recovered from the process gas prior to the shift stage. This heat recovery often involves steam raising in a boiler. Such boilers are prone

For purposes of comparison a commercially available copper-doped iron oxide-chrome high temperature shift catalyst was tested in a similar fashion. The results are shown in the following table.

Wet gas space velocity ( $\text{h}^{-1}$ )	Iron-free, copper-containing, catalyst				Copper-doped iron oxide-chrome catalyst			
	outlet gas CO (%)		CO/CO <sub>2</sub> ratio		outlet gas CO (%)		CO/CO <sub>2</sub> ratio	
	Initial	Retest	Initial	Retest	Initial	Retest	Initial	Retest
60000	6.4	6.9	0.9	1.0	7.0	7.3	1.1	1.2
72000	6.6	7.2	1.0	1.1	7.3	7.4	1.2	1.2
86000	6.8	7.3	1.0	1.2	-	7.7	-	1.3
98000	7.0	7.7	1.1	1.3	7.6	7.8	1.3	1.4
110000	-	7.9	-	1.4	7.9	8.0	1.4	1.5

From the above results it is seen that the iron-free, copper-containing, preliminary shift catalyst was effective, even at high wet gas space velocities, to effect sufficient conversion of carbon monoxide to decrease the carbon monoxide to carbon dioxide ratio to below 1.9 and so it would be possible to replace the initial part, less than 5% by volume, of a conventional iron oxide-containing high temperature shift catalyst operating at a wet gas space velocity of 5000  $\text{h}^{-1}$  by the iron-free, copper containing, preliminary shift catalyst and effect sufficient conversion of carbon monoxide before the gas encountered the iron oxide-containing catalyst.

#### Example 2

In this example a precursor to an iron-free, copper-containing, catalyst was prepared using a macroporous alumina foam as a support. The support was in the form of cylindrical pellets of 16 mm diameter and 16 mm height having a porosity of 35-40% and a density of about 1.3  $\text{g/cm}^3$  and was made by the process described in US 4 810 685. The precursor was made by dipping the pellets in a slurry containing about 40% by weight of co-precipitated copper, zinc and aluminium compounds in the approximate atomic proportions of 3.4 Cu : 1.7 Zn : 1 Al. The impregnated support was dried and calcined at 380 to 420°C to decompose the copper, zinc and aluminium compounds to the corresponding oxides. The resulting copper-containing foam pellets contained 1.42% by weight of copper.

45 ml of the copper containing foam pellets, i.e. containing a total of 0.59 g of copper, were crushed and mixed with 155 ml of alpha-alumina chips and charged to a tubular reactor of internal diameter 37 mm. The copper oxide in the pellets was reduced to metallic copper by passing the test gas as used in Example 1 but containing 50 parts by volume of steam per 50

Wet gas space velocity ( $\text{h}^{-1}$ )	outlet gas CO (%)			CO/CO <sub>2</sub> ratio		
	Initial	Retest	after wetting	Initial	Retest	after wetting
20000	3.6	5.2	6.3	0.4	0.6	0.9
24000	3.8	5.6	-	0.4	0.7	-
28000	4.2	5.8	-	0.5	0.8	-
32500	4.7	6.0	-	0.5	0.8	-
37000	4.4	6.3	-	0.5	0.9	-

#### Example 4

Example 2 was repeated but instead of using a slurry of the copper, zinc and aluminium compounds, the latter were homogeneously precipitated in the presence of the foam pellets by dipping the foam pellets into an aqueous solution containing copper, zinc and aluminium nitrates and urea. The solution was made up by adding 212.85 g of urea to 500 ml of an aqueous solution containing 302 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 145.77 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 48.77 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ .

The excess of the solution was drained from the pellets and then the latter were calcined at 450°C. The pellets contained 4.38% by weight of copper. 25 ml of the copper containing foam pellets, containing a total of 0.92 g of copper, were crushed and mixed with 175 ml of alpha-alumina chips and charged to a tubular reactor of internal diameter 37 mm. The copper oxide in the pellets was reduced to metallic copper by passing the test gas as used in Example 1 but containing 50 parts by volume of steam per 50 parts of dry gas at a pressure of 28 bar abs. The reduction was initiated at 250°C, and the temperature was increased gradually to 440°C and held at that temperature for 4 hours. The amount of steam in the test gas was then decreased to 50 parts by volume of steam per 100 parts of dry gas.

The temperature was decreased to 365°C and the space velocity (litres of wet gas per litre of undiluted catalyst per hour) was varied over a period of 5 days. The carbon monoxide content of the effluent gas, on a wet basis, was determined at various space velocities. The results are shown in the following table.

Claims.

1. A shift process wherein a gas stream containing carbon monoxide and steam is contacted with an iron oxide-containing catalyst, characterised in that, prior to contact with the iron oxide-containing catalyst, the gas stream is contacted with an iron-free, copper-containing, catalyst at an inlet temperature in the range 280-370°C.
2. A process according to claim 1 wherein the iron-free, copper-containing, catalyst is the product of reducing a support impregnated or coated with a copper compound.
3. A process according to claim 2 wherein the iron-free, copper-containing catalyst contains 3 to 15% by weight of copper.
4. A process according to any one of claims 1 to 3 wherein the inlet temperature is in the range 280-330°C.
5. A process according to any one of claims 1 to 4 wherein the iron-free, copper-containing, catalyst is operated at a wet gas space velocity of at least 50000 h<sup>-1</sup>.
6. A process according to any one of claims 1 to 5 wherein the amount of iron-free copper-containing catalyst is such that the wet gas flow rate is in the range 250-3000 litres (at NTP) of wet gas per g of copper in the catalyst per hour.
7. A process according to any one of claims 1 to 6 wherein the gas fed to the iron-free, copper-containing, catalyst contains hydrogen and carbon dioxide in addition to carbon monoxide and steam and has a carbon monoxide to carbon dioxide molar ratio above 1.9.
8. A process according to any one of claims 1 to 7 wherein the gas fed to the iron-free, copper-containing, catalyst has a steam to dry gas ratio in the range 0.2 to 0.6.
9. A process according to any one of claims 1 to 8 wherein the iron-free, copper-containing, catalyst effects conversion of 5 to 15% of the carbon monoxide in the gas fed to the iron-free, copper-containing, catalyst.

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